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Continuum Approximation of Large Reaction Mixtures in Reactors with Backmixing

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The growing need to produce ultraclean fuels from hydrocarbon mixtures such as petroleum fractions and residues has put increasing pressure on refiners to achieve deep conversions. It is imperative to be able to predict the behavior of such mixtures at high conversions as functions of their properties and reactor type. To this end, treating the reaction mixture as a continuum greatly simplifies the analysis and modeling of the conversion process. However, the continuum approximation can become invalid at very high conversions. Previously, we examined the validity of the approximation for various reactions in plug flow reactors. The validity conditions for first-order reaction mixtures in reactors with different mixing intensities are developed. In general, backmixing widens the range of validity. In certain cases, the continuum approximation is valid at arbitrarily high conversions. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 159–165, 2015

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Introduction

The energy industry has been and will continue to rely on hydrocarbon-based feedstocks in the coming decades. Large, complex hydrocarbon mixtures such as crudes, petroleum fractions, coal liquids, tight oils have an astronomically large number of chemical species. In many situations, one is mainly interested in the collective, rather than the individual, behavior of the reacting species. For instance, in hydrodesulfurization (HDS), only the reduction of total sulfur really matters. The same is true of hydrodenitrogenation (HDN) and hydrodemetallation. Fluid catalytic cracking (FCC) is designed primarily for the deep conversion of high-boiling (>340°C) to low-boiling (<340°C) fractions.

The problem of finding the collective behavior and overall, lumped kinetics of a large number of reactions can be stated as follows. Let $c_i(t)$ $(i = 1, 2, \cdot\cdot, N >> 1)$ be the concentration of reactant i with rate constant k_i and $C(t) = \Sigma_i c_i$ be the total concentration of all reactants at reactor residence time t. The concentration of reactant i in the feed is $c_{if} = c_i(0)$. Each reactant disappears at its own rate r_i. The aim is to predict the dependence of $C(t)$ on feed properties and reactor type. It is also of interest to know if an overall, lumped kinetics $\bar{r}(C)$ can be found for the large mixture as a whole.[1] To this end, a mathematically convenient approach is to treat the mixture as a continuum.[2–5] That is, the sum Σ_i is replaced by an integral over a distribution function, which is parameterized by a small number of constants. In practice, chemical-analytical characterization data for hydrocarbon mixtures are often obtained as a continuous function of one or more macroscopic properties such as boiling point, molecular weight, or hydrogen deficiency. In many refining processes, hydrocarbon's reactivity is closely related to boiling point (or molecular size) and hydrogen deficiency. It can also be used to solve an inverse problem: determining feedstock reactivity-composition spectra from the measured $C(t)$.[6] Examples of continuum process models can be found elsewhere.[7–9]

For the design and development of hydrocarbon conversion catalysts and processes, it is important to determine $C(t)$ and $\bar{r}(C)$ *a priori*, which requires complete information on feed properties and reactivity spectra. In practice, however, practitioners do not usually have the luxury of fully charactering hydrocarbon feedstocks. A pragmatic approach is to find $C(t)$ and $\bar{r}(C)$ at high conversions (or long time) for partially characterized feedstocks.[10–12] Such an asymptotic approach provides a simple, unifying framework for gaining insights into a mixture's behavior and explaining many perplexing behaviors observed in hydrocarbon processing.[1] A remarkable result of a recent study is that the long-time (high conversion) behavior of a reaction mixture with nonlinear kinetics (i.e., power-law) is not necessarily dominated by the most refractory species. It actually can be dominated by species of intermediate reactivity, moderately refractory species, or all species.[13]

Developing long-time asymptotic kinetics is commensurate with the growing need of refiners to achieve deep conversions, which is mainly driven by the ever-increasing demand for ultraclean fuels. For example, the diesel sulfur specifications in a few countries are now set at 10–15 ppmw. More countries will certainly follow suit in the near future. The sulfur content of middle distillates (200–370°C boiling

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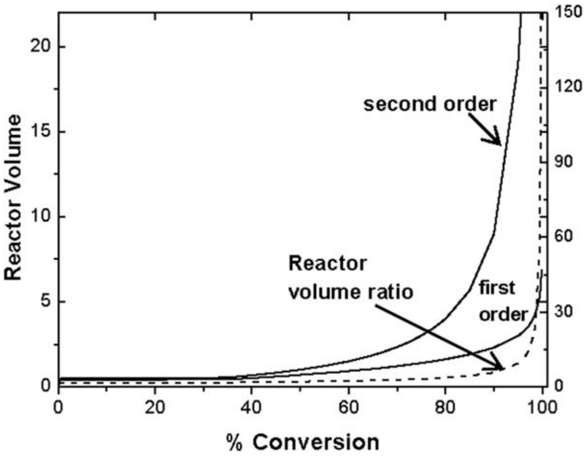

Figure 1. Reactor volume and reactor volume ratio vs. percent conversion for first- and second-order reactions.

range) typically ranges between 1 and 3 wt %. Desulfurizing a distillate from 1 wt % sulfur to 10 ppmw means an HDS level of 99.9%. A similar situation exists in hydrocracking which requires ultradeep HDN. In exploring or developing new catalysts for hydroprocessing, it is important that competing catalysts are evaluated at high conversions. With the dwindling supply of light/sweet crudes, irrefrangible feedstocks (e.g., vacuum residues, heavy oils, bitumen, etc.) and unconventional feedstocks (shale/tight oils, biomass, etc.) will play an increasingly important role. To fully use these emerging, difficult-to-treat feedstocks requires deep conversion processes. This may incur huge capital outlays because reactor volume is extremely sensitive to conversion at high conversions. This is shown in Figure 1 for first- and second-order reactions in an isothermal plug-flow reactor (PFR). Also shown is the reactor volume ratio for the two reactions vs. percent conversion, which illustrates the importance of knowing the deep-conversion kinetics. Various multiphase reactors with a wide range of backmixing intensities have been used for catalyst and process development. For example, slurry bubble column reactors containing finely dispersed catalysts are used for upgrading heavy, residual oils.[14] To achieve ultradeep conversions without increasing the reactor volume requires the use of a recycle reactor. Recycle-to-extinction reactors are used to obtain the last drop of liquid from bottom-of-barrel hydrocarbons.[15,16]

Useful as it may be, the long-time asymptotic analysis based on the continuum theory has its limitation.[17] Consider first-order reactions in a discrete mixture as an example. After a sufficiently long time, one expects that the mixture behaves as if there were only one surviving reactant decaying exponentially because the concentrations of all other species are exponentially smaller. However, the corresponding continuous mixture at large times decays asymptotically as a second-order reaction.[18] This apparent paradox arises from the fact that the long-time asymptotic kinetics is valid only over an intermediate time frame—one in which time is long enough for the asymptotic kinetics to be valid (and the mixture's behavior no longer depends on the details of feed properties), but short enough for the mixture remaining to be sufficiently crowded (hence second-order kinetics). Such intermediate asymptotics are common in a variety of physicochemical systems.[19]

Recently, an important finding is that for some reaction mixtures the continuum approximation can actually be valid for arbitrarily long times.[13] This finding prompted us to further investigate the validity range of the continuum approximation for different deep-conversion processes. Specifically, the present work examines the effect of backmixing on the validity conditions for first-order reaction mixtures in a plug flow reactor with recycle.

Plug Flow Reactor

When the total number of species N is very large, we may approximate a discrete mixture for which $C(t) = \Sigma_i c_i$ by a continuous mixture with[5]

$$C(t) = \int_{\mathrm{o}}^{\infty} \tilde{c}(k,t) D(k) dk \tag{1}$$

Here, each reactant is labeled by its reactivity k. The concentration of reactant k is $\tilde{c}(k,t)$. The slice $D(k)dk$ is the total number of reactant types with rate constant between k and $k + dk$. Thus, D is a reactant-type distribution function and acts as the Jacobian of the discrete-to-continuous (i-to-k) coordinate transformation.[5] The construction of $D(k)$ requires analytical measurements[20,21] combined with kinetics experiments using representative model compounds.[22,23] The number of identifiable species depends on the specific refining process and available analytical capabilities. It has been reported that $N \sim 3000$ for FCC.[24]

The large reaction mixture at hand can be normalized as follows[12]

$$\begin{aligned} &U = C(t)/C_o, c(x,t) = \tilde{c}(k,t)/\hat{c}, x = k/\hat{k} \\ &f(x) = c_f(k)/\hat{c}, g(x) = \hat{k}D(k)/N, \tau = \hat{k}t \end{aligned} \tag{2}$$

where U and τ are the dimensionless total concentration and residence time, respectively. Also, $C_{\mathrm{o}} = C(0) = N\hat{c}$ and $\hat{k}$ is a characteristic rate constant for a moderately refractory species with the average feed concentration $\hat{c}$. The subscript f signifies feed. A reactant with a small x is refractory; the closer its x value is to zero, the more refractory is the reactant.

The above scaling leads to the following normalization conditions

$$\int_0^{\infty} f(x) g(x) dx = \int_0^{\infty} g(x) dx = 1 \tag{3}$$

We consider the case where the behaviors of $g(x)$ and $f(x)$ near $x = 0$ are expressible as

$$f(x) = x^{v}(f_0 + f_1 x + \cdots) \sim f_0 x^{v} \tag{4}$$

$$g(x) = x^{\mu}(g_0 + g_1 x + \cdots) \sim g_0 x^{\mu} \tag{5}$$

where $v \geq 0$ and $1 + \mu > 0$. If the feed has a finite amount of unconvertible species, $\mu = v = 0$. When $\mu \leq 0$, the mixture has a finite number of reactant types that are virtually unreactive. An important parameter emerges is $\gamma \equiv 1 + \mu + v$, which is a measure of the overall reactivity of the feed. A small γ implies a refractory feed.

We let $h(x) = f(x)g(x) \geq 0$, so $h(x) \sim h_0 x^{\gamma - 1}$ near $x = 0$ with $h_0 = f_0 g_0$. As shown before, the large-τ behavior of a first-order reaction mixture in a PFR is[12,17]

$$U_{\mathrm{c}}(\tau) = \int_0^{\infty} h(x) \mathrm{e}^{-x\tau} dx \sim \frac{h_0 \Gamma(\gamma)}{\tau^{\gamma}} \text{as} \tau \to \infty \tag{6}$$

The subscripts c and d denote continuous and discrete mixtures, respectively. Each constituent species in the

Table 1. Validity Conditions for Different Cases: $\bar{\tau} \equiv \tau/(1+R)$

Case	U's Leading-Order Term	Validity Condition
Base Case: $R=0$	$\frac{h_o\Gamma(\gamma)}{\tau^\gamma}$	$\tau\delta \ll 1$
A: $\tau \to \infty$, R finite	$\frac{h_o(1+R)^\gamma}{\tau^\gamma}\int_0^\infty \frac{x^{\gamma-1}e^{-x}dx}{1+R(1-e^{-x})}$	$\tau\delta \ll 1+R$
B1 : $R \to \infty, \tau \to \infty,$ $0<\gamma<1$	$\frac{h_o\Gamma(\tau)\Gamma(1-\gamma)}{\tau^\gamma}$	$\tau\delta \ll 1$
B2 : $R \to \infty, \tau \to \infty$ $\gamma > 1, \bar{\tau} \to 0$	$\frac{1}{\tau}\int_0^\infty \frac{h(x)dx}{x}$	$\delta \ll 1$
B3 : $R \to \infty, \tau \to \infty$ $\gamma=1, \bar{\tau} \to 0$	$\frac{h_o \ln\tau}{\tau}$	$\frac{\tau\delta}{\ln\tau} \ll 1$
C1 : $R \to \infty, \tau \to \infty$ $\gamma > 1, \bar{\tau} \to \infty$	$\frac{h_o R^{\gamma-1}}{\tau^\gamma}\int_0^\infty \frac{x^{\gamma-1}dx}{(e^x-1)}$	$\tau\delta \ll R$
C2 : $R \to \infty, \tau \to \infty$ $\gamma > 1, \bar{\tau} \to \tau^* > 0$	$\frac{1}{R}\int_0^\infty \frac{h(x)dx}{(e^{x\tau^*}-1)}$	$\delta \ll 1$
C3 : $R \to \infty, \tau \to \infty$ $\gamma=1, \bar{\tau} \geq \bar{\tau}_b > 0$	$\frac{h_o \ln R}{\tau}$	$\tau\delta \ll \ln R$

corresponding discrete mixture decays as $c_i = c_{if}\exp(-k_i t)$. Let Δ be the maximum difference between the rate constants for two species whose reactivities are adjacent to each other, that is, $\Delta \equiv \max_i\{k_{i+1}-k_i\} > 0$. For simplicity, we assume all the rate constants are equally spaced so that $\Delta=\hat{k}\delta$ and $x_i=i\delta$.

It can be shown that the relation $U_d \sim U_c$ requires a sufficiently fine granularity so that δ goes to zero faster than τ goes to infinity.[17] That is

$$\tau\delta \to 0 \text{ as } \delta \to 0 \text{ and } \tau \to \infty \tag{7}$$

Alternative forms of Eq. 7 are $\tau\delta \ll 1$ and

$$\frac{1}{\hat{k}} \ll t \ll \frac{1}{\Delta} \tag{8}$$

Equation 8 says that time cannot be too long without the underlying discreteness of the mixture manifesting itself. To apply the above criteria to the HDS of diesel fuel, one can use the model-compound data of Houalla et al. on the HDS of dibenzothiophenes over a sulfided Co-Mo/γ-Al_2O_3 catalyst.[22] The grid size Δ can be estimated from the first-order rate constants for 4-methyl-dibenzothiophene and 4,6-dimethyl-dibenzothiophene. The rate constant for the HDS of dibenzothiophene can be used as $\hat{k}$. In this case, the validity condition shown in Eq. 8 is not very stringent under the conditions used.[17]

To include more reaction classes, Eq. 8 can be generalized into a power-law form as follows[13]

$$\frac{1}{\hat{k}} \ll t \ll \left(\frac{\hat{k}}{\Delta}\right)^y \frac{1}{\hat{k}} \text{ or } \left(\frac{\hat{k}}{\Delta}\right)^y \gg 1 \tag{9}$$

The exponent y depends on reaction kinetics and feed properties (μ, v). For irreversible first-order reactions, reversible first-order reactions, and bimolecular second-order reactions, $y = 1$, 2, and 3, respectively.[13] Here, the mixtures can be called nonuniform in that their long-time behaviors are dominated by a subset of reactants.[13] In this case, time cannot be arbitrarily long. In sharp contrast, the continuum approximation can actually be valid for arbitrarily long time. One such example is nth-order reactions with $n > 1 + 1/(1+\mu)$. Mixtures of this type are uniform in that their long-time behaviors are governed by all species. Zeroth and fractional order reactions, $n \leq (1 - 1/v)$, are incompatible with continuum description.[13]

We now proceed with the development of validity conditions for first-order reactions in reactors with varying degrees of backmixing intensities.

Plug Flow Reactor with Recycle

Classification of backmixing intensity

For an isothermal PFR with a recycle ratio R, U_c takes the form

$$U_c(\tau) = \int_0^\infty \frac{h(x)e^{-x\tau/(1+R)}dx}{1+R(1-e^{-x\tau/(1+R)})} \tag{10}$$

Here, R is the ratio of the fluid volume returned to the reactor entrance to the fluid volume leaving the reactor: the larger the R, the higher the backmixing intensity. The two ideal reactors, PFR and continuous stirred tank reactor (CSTR), correspond to $R = 0$ and $R \to \infty$, respectively. Here, R is a measure of mixing intensity, with all the nonideal complexities represented by $0 < R < \infty$. For recycle reactors, Eq. 10 indicates a characteristic time scale $\bar{\tau}$ defined as

$$\bar{\tau} \equiv \frac{\tau}{1+R} \tag{11}$$

The corresponding discrete version of Eq. 10 takes the form

$$U_d(\tau) = \sum_{i=1}^{\infty} \frac{h(i\delta)e^{-i\delta\tau/(1+R)}\delta}{1+R(1-e^{-i\delta\tau/(1+R)})} \tag{12}$$

For fixed τ, as $\delta \to 0$, U_c is a satisfactory approximation to U_d as Eqs. 10 and 12 are the definition of the Riemann integral in elementary calculus.

We now look into the asymptotic behaviors of U_c and U_d as $\tau \to \infty$ for reactors with a range of backmixing intensities ($0 \leq R \leq \infty$). To this end, it is helpful to consider the following large-τ cases: (A) mildly backmixed reactors for small or intermediate R with $\bar{\tau} \to \infty$, (B) completely backmixed reactor (i.e., CSTR) with $R \to \infty$ and $\bar{\tau} \to 0$, and (C) highly backmixed reactors for large R with $\bar{\tau} \to$ finite > 0 or $\bar{\tau} \to \infty$. For ease of classification, Case A may be broadly viewed as a near-PFR system, whereas Case C is a near-CSTR system. Although the derivation of the validity conditions involves considerable algebra, it is essentially an application of the Riemann integral and the dominated convergence theorem. For brevity, only one case (Case C3 in Table 1) whose derivation will be given here for illustration purposes. Table 1 gives a list of the leading-order terms of U_c and the corresponding validity conditions including the PFR base case.

To obtain U_c's long-time asymptote, it is convenient to let $x' = x\bar{\tau}$. Equation 10 can be rewritten as

$$\bar{\tau}^\gamma U_c(\tau) = \int_0^\infty \left[\bar{\tau}^{\gamma-1} h\left(\frac{x'}{\bar{\tau}}\right)\right] \frac{e^{-x'}dx'}{1+R(1-e^{-x'})} \tag{13}$$

We will invoke the dominated convergence theorem in subsequent development. Let $h(x)$ be a continuous function and $h(x) \leq Ax^{\gamma-1}$ for some A. Then

$$|\bar{\tau}^{\gamma-1} h\left(\frac{x'}{\bar{\tau}}\right)| \leq A\bar{\tau}^{\gamma-1}\left(\frac{x'}{\bar{\tau}}\right)^{\gamma-1} = Ax'^{\gamma-1} \tag{14}$$

For $\gamma > 0$, we have

$$\int_0^\infty A{x'}^{(\gamma-1)}\frac{e^{-x'}dx'}{1+R(1-e^{-x'})}<\infty \tag{15}$$

Mildly backmixed reactors: Near PFR

Recall that $h(x)\sim h_0x^{\gamma-1}$ as $x\to 0$. In the limit of $\bar\tau\to\infty$ for fixed x', we have

$$\lim_{\bar\tau\to\infty}\bar\tau^{\gamma-1}h\left(\frac{x'}{\bar\tau}\right)\to\bar\tau^{\gamma-1}h_0\left(\frac{x'}{\bar\tau}\right)^{\gamma-1}=h_0(x')^{\gamma-1} \tag{16}$$

Upon taking the limit $\bar\tau\to\infty$ and for fixed R, Eq. 13 by virtue of the dominated convergence theorem becomes

$$\lim_{\bar\tau\to\infty}\bar\tau^{\gamma}U_{\mathrm{c}}(\tau)=\int_0^\infty\frac{h_o(x')^{\gamma-1}e^{-x'}dx'}{1+R(1-e^{-x'})} \tag{17}$$

Rewriting the dummy variable x' as x, we have for $\bar\tau\to\infty$ and finite R that

$$U_{\mathrm{c}}(\tau)\sim\frac{h_o}{\bar\tau^{\gamma}}\int_0^\infty\frac{x^{\gamma-1}e^{-x}dx}{1+R(1-e^{-x})}\equiv\frac{p_c}{\bar\tau^{\gamma}} \tag{18}$$

Here, p_c depends on R, h_o, and γ. The presence of h_o signals that the mixture's long-time behavior is governed by the most refractory species. For $\bar\tau\to\infty$, U_{c} decays asymptotically in a power-law fashion, which has the same structure as Eq. 6 for a PFR. It can be shown that the validity condition shown in Eq. 7 can be applied to the recycle reactor with finite R here. Replacing τ with $\bar\tau$ in Eq. 7, we obtain the following validity condition for Case A shown in Table 1, that is, $\bar\tau\delta\to 0$ or $\tau\delta/(1+R)\to 0$ as $\tau\to\infty$ In other words

$$\tau\delta\ll 1+R\ \text{for all}\ \gamma \tag{19}$$

which should be compared with the condition $\tau\delta\ll 1$ for the PFR case. This result indicates that the recycle-induced backmixing widens the validity range of the continuum approximation. Equation 18 implies that here the overall, lumped asymptotic kinetics is of the power-law form shown below

$$\frac{dU_{\mathrm{c}}}{d\bar\tau}\sim\bar r(U_{\mathrm{c}})=-(\frac{\gamma}{p_c})U_{\mathrm{c}}^{1+1/\gamma} \tag{20}$$

Equation 20 shows that the overall rate constant $(-\gamma/p_c)$ depends on the feed properties and the recycle ratio R. The analyses of discrete mixtures by Luss and Hutchinson indicated that the overall kinetics are different for a plug flow reactor with and without recycle.[25,26]

Completely backmixed reactors: CSTR

Here, we first take the limit of $R\to\infty$ in Eq. 10 so the reactor in a completely backmixed state. The resulting mass balance equation is of the following form which does not have an exponential term

$$U_{\mathrm{c}}(\tau)=\int_0^\infty\frac{h(x)dx}{(1+\tau x)} \tag{21}$$

We next take the $\tau\to\infty$ limit to obtain the long-time asymptote. Analogous to the previous developments,[12] it can be shown that there are three asymptotics depending on the feed reactivity parameter γ.

1. $0<\gamma<1$

$$U_{\mathrm{c}}\sim\frac{h_o\Gamma(\gamma)\Gamma(1-\gamma)}{\tau^{\gamma}}\ \text{as}\ \tau\to\infty \tag{22}$$

Here the long-time asymptotic behavior is governed by refractory species, so the mixture is nonuniform.[13] Moreover, Eq. 22 shows the same power-law decay behavior as Eq. 6. It can be shown that the validity conditions shown in Eqs. 7 and 8 can be applied to this case. That is, $\tau\delta\to 0$ as $\delta\to 0$, $\tau\to\infty$, and $\bar\tau\to 0$. This condition, listed as Case B1 in Table 1, is valid regardless of the order of taking the limits of $\tau\to\infty$ and $R\to\infty$.

2. $\gamma>1$

$$U_{\mathrm{c,CSTR}}(\tau)\sim\frac{1}{\tau}\int_0^\infty\frac{h(x)dx}{x}\ \text{as}\ \tau\to\infty \tag{23}$$

This highly reactive ($\gamma>1$) mixture is uniform as its long-time behavior is governed by all species. So, the continuum approximation is valid at all times as long as $\delta<<1$, which is listed as Case B2 in Table 1, corresponding to the limits $\tau\to\infty$, $R\to\infty$, and $\bar\tau\to 0$. This case is similar to the high-order reaction mixture (irreversible *n*th-order with $n>1+1/[1+\mu]$) discussed previously.[13]

3. $\gamma=1$

$$U_{\mathrm{c,CSTR}}(\tau)\sim\frac{h_0\ln\tau}{\tau}\ \text{as}\ \tau\to\infty \tag{24}$$

This nonuniform mixture marks the transition from all-species-dominated mixture ($\gamma>1$) to refractory-species-dominated mixture ($\gamma<1$). It can be shown that the validity condition becomes (Case B3 in Table 1)

$$\frac{\tau\delta}{\ln\tau}\ll 1\ \text{as}\ \tau\to\infty \tag{25}$$

The above condition is valid as long as $\bar\tau\to 0$ when $\tau\to\infty$ and $R\to\infty$.

Highly backmixed reactors

For Case C discussed here, R is allowed to be very large, but not large enough to make $\bar\tau\to 0$. Instead, $\bar\tau\to\infty$ or $\bar\tau\to$ finite$\,>0$ as $R\to\infty$. Here, when the continuum approximation is conditionally valid, the validity conditions depend on R. Moreover, as can be seen from Table 1, the validity conditions for Case C bear some resemblance to those in Cases B and A. As an example, for feed mixtures with $\gamma>1$ in Cases B2 ($\bar\tau\to 0$) and C2 ($\bar\tau\to$ finite$\,>0$), the large-τ behaviors are governed by all species. So, the continuum approximation is valid at all times as long as $\delta<<1$. Also, the validity conditions for Cases C1 and A are similar.

In what follows, we derive the validity condition for the $\gamma=1$ case under the limiting conditions $\tau\to\infty, R\to\infty$, and $\bar\tau\geq\bar\tau_b>0$. When $\gamma=1$, $h(x)\to h_o$ as $x\to 0$. Equation 10 can be rewritten as

$$I_{\mathrm{c}}\equiv\frac{R\bar\tau U_{\mathrm{c}}}{\ln(1+R)}=\int_0^\infty h(x)w_{R,\tau}(x)dx \tag{26}$$

where

$$w_{R,\tau}(x)\equiv\frac{R\bar\tau e^{-x\bar\tau}}{\ln(1+R)[1+R(1-e^{-x\bar\tau})]} \tag{27}$$

Here, the mass balance equation retains some PFR character through the exponential term. The discrete counterpart, Eq.12, takes the form

$$I_{\mathrm{d}}\equiv\frac{R\bar\tau U_{\mathrm{d}}}{\ln(1+R)}=\sum_{i=1}^{\infty}h_i(i\delta)w_{R,\tau}(i\delta)\delta \tag{28}$$

It can be shown that

$$\int_0^x w_{R,\tau}(x')dx' = \frac{\ln\left[1+R(1-e^{-x\bar{\tau}})\right]}{\ln(1+R)} \equiv z \tag{29}$$

In terms of the new variable z, I_c can be expressed as follows

$$I_c \equiv \int_0^1 h[x_{R,\tau}(z)]dz \tag{30}$$

where

$$x_{R,\tau}(z) = -\frac{\ln\left\{1-\left[(1+R)^z-1\right]/R\right\}}{\bar{\tau}} \tag{31}$$

As $\tau \to \infty, R \to \infty$, and $\bar{\tau} \geq \bar{\tau}_b > 0$, we have

$$x_{R,\tau}(z) \to 0 \quad 0 \leq z < 1 \tag{32}$$

Since $h(x)$ is bounded and continuous as $x \to 0$, the dominated convergence theorem gives that

$$\lim I_c = \int_0^1 h(0)dy = h_o \tag{33}$$

Therefore, $I_c \sim h_o$ and from Eq. 26

$$U_c \sim \frac{h_o \ln(1+R)}{R\bar{\tau}} \sim \frac{h_o \ln R}{\tau} \tag{34}$$

We now consider I_d. Let x_o be arbitrary and define the greatest integer J as

$$J = \left[\left|\frac{x_o}{\delta}\right|\right] \tag{35}$$

Thus, J is an integer and $J\delta \leq x_o \leq (J+1)\delta$. Note that $w_{R,\tau}$ is non-negative and monotone decreasing. Referring to Figure 2, we obtain via the lower Riemann sums that

$$\begin{aligned}\sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta &< \int_0^{J\delta} w_{R,\tau}(x)dx \leq \int_0^{x_o} w_{R,\tau}(x)dx \\ &= \frac{\ln\left[1+R(1-e^{-x_o\tau})\right]}{\ln(1+R)}\end{aligned} \tag{36}$$

Taking the upper limit (or limit superior), we have

$$\lim\ \sup \sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta \leq 1 \tag{37}$$

Also, by considering the upper Riemann sums, depicted in Figure 3, we have

$$\begin{aligned}\int_0^{x_o} w_{R,\tau}(x)dx - \int_{J\delta}^{x_o} w_{R,\tau}(x)dx = \int_0^{J\delta} w_{R,\tau}(x)dx &< \sum_{i=0}^{J-1} w_{R,\tau}(i\delta)\delta \\ &\leq \sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta + w_{R,\tau}(0)\delta\end{aligned} \tag{38}$$

so that

$$\sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta \geq \int_0^{x_o} w_{R,\tau}(x)dx - 2w_{R,\tau}(0)\delta \tag{39}$$

where

$$w_{R,\tau}(0)\delta = \frac{R\bar{\tau}\delta}{\ln(1+R)} \tag{40}$$

Equation 39 becomes

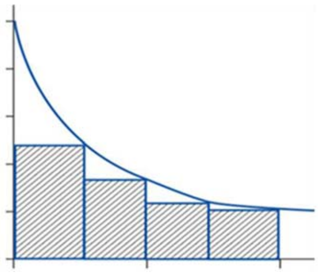

Figure 2. Lower Riemann sum for a non-negative monotone decreasing function.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta \geq \frac{\ln\left[1+R(1-e^{-x_o\bar{\tau}})\right]}{\ln(1+R)} - \frac{2R\bar{\tau}\delta}{\ln(1+R)} \tag{41}$$

If we assume the following validity condition for $\tau \to \infty$, $R \to \infty$, and $\bar{\tau} \geq \bar{\tau}_b > 0$

$$\frac{R\bar{\tau}\delta}{\ln(1+R)} \sim \frac{\tau\delta}{\ln R} \to 0 \tag{42}$$

then the lower limit (or limit inferior) is

$$\lim\ \inf \sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta \geq 1 \tag{43}$$

Combining Eqs. 37 and 43, we obtain under the limiting conditions

$$\lim \sum_{i=1}^{J} w_{R,\tau}(i\delta)\delta = 1 \tag{44}$$

For the special case $x_o \to \infty$,we get

$$\lim \sum_{i=1}^{\infty} w_{R,\tau}(i\delta)\delta = 1 \tag{45}$$

It follows from the above two equations that for finite x_o

$$\lim \sum_{i=J+1}^{\infty} w_{R,\tau}(i\delta)\delta = 0 \tag{46}$$

Now, let ε be arbitrarily small and choose x_o such that $|h(x)-h_o| < \varepsilon$ when $0 \leq x \leq x_o$. Let

$$I_d = \bar{I}_d + \tilde{I}_d + \hat{I}_d \tag{47}$$

where

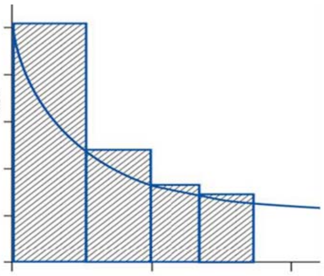

Figure 3. Upper Riemann sum for a non-negative monotone decreasing function.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\bar{I}_{\mathrm{d}}=\sum_{i=1}^{J} h_o w_{R,\tau}(i\delta)\delta \tag{48}$$

$$\tilde{I}_{\mathrm{d}}=\sum_{i=1}^{J}[h(i\delta)-h_o]w_{R,\tau}(i\delta)\delta \tag{49}$$

$$\hat{I}_{\mathrm{d}}=\sum_{i=J+1}^{\infty} h(i\delta)w_{R,\tau}(i\delta)\delta \tag{50}$$

It can be shown from Eq. 44 that

$$\lim\sup|\bar{I}_{\mathrm{d}}-h_o|=\lim h_o\left|\sum_{i=1}^{J} w_{R,\bar{\tau}}(i\delta)\delta-1\right|=0 \tag{51}$$

It then follows that

$$\lim \bar{I}_{\mathrm{d}}=h_o \tag{52}$$

The corresponding limits for $\tilde{I}_{\mathrm{d}}$ and $\hat{I}_{\mathrm{d}}$ become arbitrarily small, that is

$$\lim\ \sup \tilde{I}_{\mathrm{d}} \le \lim\ \sup \sum_{i=1}^{J}|h(i\delta)-h_o|w_{R,\tau}(i\delta)\delta \le \varepsilon \tag{53}$$

$$\lim\sup|\hat{I}_{\mathrm{d}}| \le \sup_x\ |h(x)|\lim \sum_{i=J+1}^{\infty} w_{R,\tau}(i\delta)\delta=0 \tag{54}$$

So $\lim\sup\ |I_{\mathrm{d}}-h_o| \le \varepsilon$. As ε is arbitrarily small, in the limits mentioned above

$$\lim I_{\mathrm{d}} \sim h_o \tag{55}$$

The result is that

$$U_{\mathrm{d}} \sim \frac{h_o \ln(1+R)}{R\bar{\tau}} \sim \frac{h_o \ln R}{\tau} \tag{56}$$

provided that Eq. 42 holds true, that is, $\tau\delta \ll \ln R$.

Concluding Remarks

The need to achieve deep conversion of heavy oils, residues, and nonconventional oils will certainly grow in the coming years. The continuum approach plays an increasingly important role as the number of chemical species in hydrocarbon feedstocks increases exponentially with their heaviness. Although the approach offers a practical tool for analysis and modeling of deep-conversion processes, it is imperative to determine the condition under which the continuum approximation and its deep-conversion limit are both valid. The adequacy of the approximation depends on kinetics, feed properties, reactor type, and pore diffusion. Previously, we showed that the behavior of complex feedstocks at deep conversions can depend on all species, species of intermediate reactivity, moderately refractory species, or refractory species. In this study, we address the adequacy of the approach for reactors that are mildly, highly, or completely backmixed.

The validity conditions for the continuum approximation in most cases become less stringent on introducing backmixing in the reactor. The application of the continuum approximation will continue to benefit from advances in analytical techniques for molecular speciation analyses of complex mixtures. The results obtained from the present study will help pinpoint where the emphasis should be in this endeavor.

Notation

c_i = concentration of ith species
c_{if} = concentration of ith species in the feed
$\hat{c}$ = average feed concentration
$\tilde{c}(k,t)$ = concentration of k species in the continuous mixture
$c(x,t)$ = dimensionless concentration of species in the continuous mixture
$c_f(k)$ = feed concentration of k species in the continuous mixture
C = total concentration of all reactants
C_{o} = total concentration at time = 0
D = reactant type distribution function, Eq. 1
f = dimensionless feed concentration function, Eq. 2
f_o = constant in feed distribution function, Eq. 4
g = dimensionless reactant type distribution function, Eq. 2
g_o = constant in reactant type distribution function, Eq. 5
h = function defined as $h \equiv fg$
k = rate constant or label for continuous mixture
$\hat{k}$ = characteristic rate constant
N = total number of reactant types
p_c = function defined in Eq. 17
$\bar{r}$ = overall apparent kinetics for reaction mixtures as a whole
R = recycle ratio
r_i = reaction rate for the ith reactant
t = reaction time
U = dimensionless total concentration
U_{c} = dimensionless total concentration in continuous mixture
U_{d} = dimensionless total concentration in discrete mixture
x = dimensionless rate constant, $x \equiv k/\hat{k}$
z = variable defined in Eq. 29

Greek letters

γ = constant defined as $\gamma \equiv 1+\mu+v$
Δ = reactivity granularity defined as $\Delta \equiv \max_i\{k_{i+1}-k_i\} > 0$
δ = dimensionless reactivity granularity, $\delta \equiv \Delta/\hat{k}$
τ = dimensionless time defined in Eq. 2
$\bar{\tau}$ = dimensionless time defined as $\bar{\tau}=\tau/(1+R)$
$\bar{\tau}_b$ = a finite, positive number

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